SNC

PRELIMINARY INVESTIGATION

DESULPHURIZATION OF HYDROCRACKED PITCH

USING

PHOSPHORUS AND PHOSPHINE

REQ. NO. 0-9117

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BY

TECHNICAL DEVELOPMENT DEPARTMENT

SNC INC.

MONTREAL

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PRELIMINARY INVESTIGATION

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ABSTRACT

Preliminary experiments were carried out to explore the possibility of removing organic sulphur from hydrocracked pitch by treating it with phosphorus and phosphine at atmospheric pressure. Sulphur removal between 10 to 18% was observed. The sulphur was removed in the form of volatile organosulphur compounds, perhaps as thiophene, or as a thiophene homolog.

The increase in the phosphorus content of the residue indicates that phosphorus attaches to the pitch molecules under the experimental conditions.

1.0 INTRODUCTION

In a hydrocracking process (1) for bitumen upgrading, about 10-15 wt % higher liquid yield is achieved. However, the process also results in 5 to 10 wt. % pitch as a byproduct. To improve the economics of the upgrading process, it is desirable to utilize the hydrocracked pitch byproduct as a source of energy. The pitch has a hydrogen to carbon (H/C) atomic ratio of around 1.03. It contains sulphur (about 6 wt. %), nickel (0.04 wt. % NiO), vanadium (0.117 wt. % V_2O_5) and iron (0.6 wt. % Fe_2O_3). If it is burned, the amount of sulphur dioxide evolved would necessitate a large investment for stack-gas clean-up facility. If it is used as a feedstock for a coking process, the resulting coke will contain undesirably large concentrations of sulphur and metals. A better and less expensive approach might be to remove sulphur from pitch before burning or coking it.

Sulphur in hydrocracked pitch can be broadly grouped in two classes:

A. Inorganic Sulphur: Sulphides (FeS, CaS), disulphides (FeS_2), Sulphates ($CaSO_4$, $FeSO_4$)

B. Organic Sulphur: Thiophenes, aryl and aliphatic sulphides and aryl and alyphatic thiols.

In coal also, sulphur is present in the forms mentioned above. When coal is hydrodesulphurized (2) at 450°C and at pressure of up to 28 MPa, results indicate that only thiolic and aliphatic forms of sulphur are converted to hydrogen sulphide and removed. Sulphur removal from other functional groups when the sulphur occurs as a hetroatom in a ring structure is more difficult. The hydrocracked pitch has already undergone considerable hydrodesulphurization as a result of bitumen hydrocracking. Further removal of sulphur as hydrogen sulphide will require more severe conditions.

1.0 INTRODUCTION (cont'd)

Catalytic hydrodesulphurization in the presence of a hydrogen donor solvent also indicates that only a small fraction of the organic sulphur is removed at 400°C. This is because of a strong thermal stability of carbon-sulphur (C-S) bonds in the thiophenes and aryl sulphides. Severe reaction conditions such as high temperatures and high hydrogen pressures are needed to promote H_2S formation.

Meyers (3) suggested that phosphorus and phosphine should be capable of reducing organic sulphur to form phosphorus polysulphide and hydrogen sulphide. The standard free energy of desulphurization reactions of thiophene and thiophenol as model compounds using hydrogen and phosphine as reducing agents are shown in Table 1. Based on the criterion of negative free energy ($-\Delta F_o$) as a potential of desulphurizing power, the estimated values of $-\Delta F_o$ in Table 1 indicate that phosphine has much higher potential to desulphurize these model compounds than hydrogen.

Having recognized that phosphine might be a better desulphurizing agent for organic materials the objective of the present study was to conduct preliminary experiments to determine the extent of sulphur removal from hydrocracked pitch when treated with this reagent.

If the phosphorus or phosphine did react satisfactorily with the hydrocracked pitch it would be worthwhile to evaluate a process based on this chemical approach.

2.0 EXPERIMENTAL APPARATUS AND PROCEDURES

2.1 Phosphine Treatment

The experimental apparatus consisted of four flasks connected in series as shown in Figure 1 and Plate 1. In the first flask phosphorus was reacted with potassium hydroxide to generate phosphine, according to the reaction

$$2P_4 + 3KOH + 9H_2O \longrightarrow 5PH_3 + 3KH_2PO_4$$

The second flask acted as a droplet trap and a small gas holder.

The third flask contained the sample of pitch dissolved in toluene.

The fourth flask contained a solution of potassium hydroxide to absorb and destroy any unreacted phosphine.

Both the phosphine generating flask and the flask containing the pitch dissolved in toluene were fitted with reflux condensors.

To be able to periodically check that phosphine was indeed being generated in the first flask a by-pass containing a phosphine drager tube was installed around the second flask. To ensure that the phosphine was carried out of the generator and into the solution of pitch a slow current of nitrogen carrier gas was passed through the apparatus.

The experimental procedure was as follows:
A mixture of 10 grams of red phosphorus, 100 ml of water and 40 grams of KOH was heated to reflux under nitrogen for one hour. The phosphine gas produced was passed through 180 ml of toluene solution containing 10 grams of predissolved pitch. The temperature in the toluene flask was kept around 110°C. The unreacted phosphine gas

2.0 EXPERIMENTAL APPARATUS AND PROCEDURES

2.1 Phosphine Treatment (cont'd)

(from toluene flask) was then scrubbed through an aqueous solution of KOH to decompose phosphine before venting. After the reaction, the residue from the phosphine flask was filtered, water washed and dried to determine the amount of unreacted phosphorus.

The reacted pitch solution was divided into two parts for analysis as shown in Figure 2. The first portion was distilled under reduced pressure to remove toluene and the recovered pitch residue was analyzed for sulphur and phosphorus. To the second portion, about 100 ml of water was added. The resulting solution was heated and refluxed to decompose any phosphorus polysulfides produced during the reaction, and to hydrolyze other phosphorus derivatives present. The mixture was cooled and the organic layer separated, washed and distilled to obtain a toluene-free product residue. The separated aqueous layer was analyzed for the presence of sulfide and phosphate ions. The residue was analyzed for sulphur and phosphorus content.

2.2 Phosphorus Treatment

A batch reaction system as shown in Figure 3 and Plate 2 was used. It consisted of a 1-litre capacity mechanically stirred 316 - stainless steel autoclave. The autoclave body contains four ports, two for introduction and removal of gases, one for temperature and one for pressure measuring guages. The heating was provided by an external flexible blanket heater of 1.2 kW capacity. The power to the heater was supplied through a voltage regulator which was used to control the autoclave temperature. The pre-fitted water cooling coil was used for cooling and agitation was provided by six-bladed flat turbine agitator. The inlet gas port was connected with a nitrogen cylinder.

2.0 EXPERIMENTAL APPARATURS AND PROCEDURES

2.2 Phosphorus Treatment (cont'd)

Nitrogen was used to purge the autoclave before the reaction and also as a carrier gas for product gases after the reaction. The gases evolved in the reaction were passed through a pressure relief valve into a flask containing methanol. A trap was installed in the exit gas line between the methanol flask and the autoclave to prevent the backflow of methanol.

The reactor was charged with 100 grams of hydrocracked pitch, 5 grams of red phosphorus and 200 ml of 5% KOH solution. In one series of experiments, the temperature maintained at 100°C. In another series of runs, the temperature was maintained at 250°C. All reactions were carried out for one hour. At the end of the reaction period, the autoclave was quickly cooled to ambient temperature. It was then purged with nitrogen and the exit gases were scrubbed with methanol.

The pitch residue remaining after the reaction was filtered, washed with water, dried thoroughly, and analyzed for its total sulphur content as described below in Section 2.3.

Blank runs were carried out under identical conditions except that red phosphorus was not introduced into the autoclave.

In many cases, a sample was withdrawn from the reactant pitch sample before reaction and analyzed for sulphur. This permitted a comparison of sulphur contents in the pitch sample just before the reaction and the product pitch residue after the desulphurization reaction.

2.0 EXPERIMENTAL APPARATUS AND PROCEDURES

2.3 Analytical

The total sulphur content in each sample before and after the experiments was determined using the Eschka Method (ASTM-D 3177) designed for the determination of sulphur in coke and coal. The presence of pyritic sulphur as FeS_2 was determined following the method of Young and Zawadzki (4). Sulphate sulphur was determined by ASTM-D 2492 method. The analysis for phosphorus as P_2O_5 was carried out using ASTM-D 3682-78 method. The sulphur and phosphorus content of samples were also analyzed by Science Industrial Research Unit of Concordia University (see Appendix A).

The methanol solution containing dissolved gases was analyzed by a Perkin-Elmer 3920 Gas Chromatograph.

The aqueous phase recovered after phosphorus treatment was tested with $Pb(NO_3)_2$ solution to determine the presence of sulphide ions. No sulphide was detected.

3.0 RESULTS AND DISCUSSION

Sulphur analysis of hydrocracked pitch is given in Table 2. The results indicate an absence of sulphate sulphur. A negligible amount (0.1%) of pyritic sulphur was found. Thus the total sulphur present in the pitch is essentially all organic sulphur.

The results of a blank experiment carried out in the absence of phosphorus are presented in Table 3. No significant change in the total sulphur content before and after the run (4.12% vs 4.02%) was observed. The GC-analysis of methanol solution did not show the presence of any dissolved hydrogen sulphide (H_2S) or SO_2 gas. These observations indicate that aqueous potassium hydroxide (KOH) alone does not desulphurize the pitch.

3.1 Desulphurization with Phosphine

The results of desulphurization experiments with phosphine gas are summarized in Table 4. In run No. 3, it was found that after 14.5% w/w of phosphorus had reacted for four hours with KOH the total sulphur in the toluene-free residue was about 3.8%. This compares with initial sulphur content of 4.68%, indicating a decrease of about 16.8% in the sulphur content. In the duplicate experiment the amount of phosphorus reacted was 13.8% w/w and the decrease in the sulphur content was around 7.8%. A comparison of the phosphorus content in the residue in runs 4 and 5 indicated that some phosphorus had reacted with the pitch.

When the product residue was hydrolyzed with water, the total sulphur content of the residue decreased by a small amount, while the phosphorus content increased substantially.

3.0 RESULTS AND DISCUSSION

3.1 Desulphurization with Phosphine (cont'd)

The phosphine concentration in the exit gas was found to be significantly lower compared to its concentration before the reaction (as judged from the length of the colored zone of a Drager tube containing silica gel impregnated with $AuCl_3$). Hydrogen sulphide (H_2S) was not found in the exit gases. These observations suggest that while the hydrocracked pitch reacts with phosphine, the sulphur in the pitch matrix is not reduced to H_2S gas. In addition phosphorus reacts with the pitch or the ash as indicated by the increase in the phosphorus content. Because neither H_2S nor phosphorus polysulphides were found either in the gas or the liquid it can only be concluded that the sulphur is being removed in the form of some volatile species such as thiophene and its derivatives along with toluene during its distillation. Toluene was distilled under vacuum (20 mm Hg) at about 70°C temperature. Thiophene and its derivatives have a sufficiently high vapor pressure to evaporate at this temperature and pressure.

The elemental analysis (6) of pitch reveals the presence of oxygen and nitrogen in addition to sulphur. These heteroatoms are organically bound and have not been reduced upon hydrocracking. The sulphur containing groups are believed to be present predominantly as thiophenes and arylsulphides which have a high thermal stability.

The increase in the phosphorus content of the residue can be explained by considering the structural aspect of the pitch matrix which is composed of high molecular weight condensed polynuclear aromatics similar to those found in asphaltenes. The asphaltenes have been shown (5) to possess acidic and basic groups which would be expected to react with PH_3 or H_3PO_4. See Appendix B, for detailed explanation.

3.0 RESULTS AND DISCUSSION

3.2 Desulphurization with Phosphorus

The reaction of phosphorus in the presence of KOH solution at 100°C indicates about 8% sulphur removal as seen from the results presented in Table 6. When similar experiments were carried out at 250°C, sulphur removal of about 10% was observed (Table 7). An analysis of aqueous phase and methanol solution did not indicate the presence of sulphide ions, phosphine or hydrogen sulphide. It has been found (11) that although phosphine gas is produced by the interaction of phosphorus with boiling KOH solution, it is also decomposed into hydrogen and phosphorus by aqueous alkaline solution and heat. The presence of both of these conditions in the autoclave suggest the possibility that phosphine gas produced in-situ, decomposed into various by-products which remained in the substrate.

In these experiments also, as reported in section 3.1, the sulphur is being removed as volatile sulphur compound.

4.0 CONCLUSIONS

The following conclusions may be drawn from the present study:

1. The sulphur in hydrocracked pitch is organic sulphur presumably present in the form of thiophenes and arylsulphides.

2. Hydrocracked pitch does react with phosphine but the sulphur is not reduced into phosphorus polysulphides or hydrogen sulphide under the conditions investigated.

3. Sulphur removal of up to 18% was observed. The mechanism appears to be one in which the phosphine reacts with the pitch and splits of a volatile fragment which contains sulphur. Probably the fragment is thiophene or a substituted thiophene.

4. The phosphorus content of the product residue increases. The phosphorus appears to be attached to the pitch matrix.

5. Phosphine dissolved in toluene probably forms phosphoric acid which reacts with basic functional groups of pitch thereby increasing phosphorus content of pitch after water refluxing.

5.0 RECOMMENDATIONS

Preliminary experiments demonstrate that phosphorus and phosphine do react with pitch under mild experimental conditions (1 bar, 100°C and 1 bar, 250°C). Sulphur is removed in the form of volatile organic compounds probably thiophene or its derivatives. Because of mild reaction conditions, only 18% sulphur removal has been achieved. However, if the reactions are carried out at higher temperature and pressure then considerably more sulphur might be removed. Therefore further investigation should be carried out to determine the effect of temperature and pressure. The choice of solvent should also be investigated.

REFERENCES

REFERENCES

1. Patmore, D.J. et al., "The CANMET Hydrocracking Process", Canada Centre for Mineral and Energy Technology (CANMET) Report ERP/ERL 78-64 (TR), August 1978.

2. Attar, A and Corcoran, W.H., Ind. Eng. Chem. - Prod. Res. Dev., 16 (2), pp.168-170, 1977.

3. Meyers, R.A. "Coal Desulphurization", Chapter 3, Marcel Dekker, New York, 1977.

4. Young, R.K. and Zawadzki, E.A., "The Determination of Pyritic Sulphur in Coal - BCR Ashing Method", Fuel, vol. 46, pp.151-152, 1967.

5. Sternberg, H.W., Raymond R., and Schweighard, F.K., "Acid-Base Structures of Coal-Derived Asphaltenes," Science, 188, 49, 1975.

6. Sekhar, M.V.C. and Ternan, M., "Pyrolysis of Pitch Derived from Hydrocracked Athabasca Bitumen", Fuel, 58, pp.92-98, 1979.

7. Sachs, H., Chem. Ber., 25, pp.1514, 1892.

8. Hartough, H.D., "Chemistry of Heterocyclic Compounds", 3, pp.454, Interscience, New York, 1952.

9. Joule, J.A. and Smith, G.F., "Heterocyclic Chemistry", Chapter 18, Van Nostrand Reinhold, London, 1975.

10. Moschopedis, S.E. and Speight, J.G., "Chemical Modification of Bitumen Heavy Ends and Their Non-Fuel Uses", paper presented at 167 ACS meeting - Division of Petroleum Chemistry, Los Angeles, California, 1974.

11. Mellor, J.W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry", volume 8, pp.809, Longmans, Toronto, 1958.

PLATES, FIGURES, AND TABLES

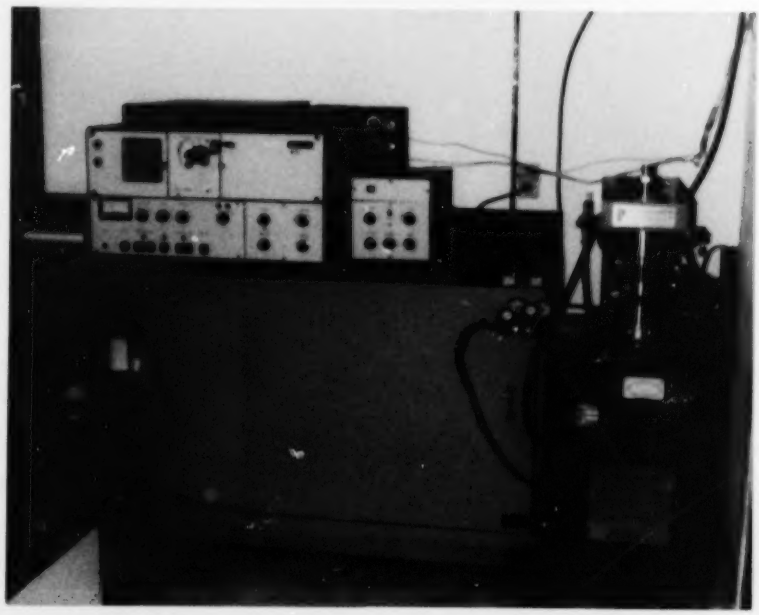


PLATE 1: Experimental Set-up Using an Autoclave

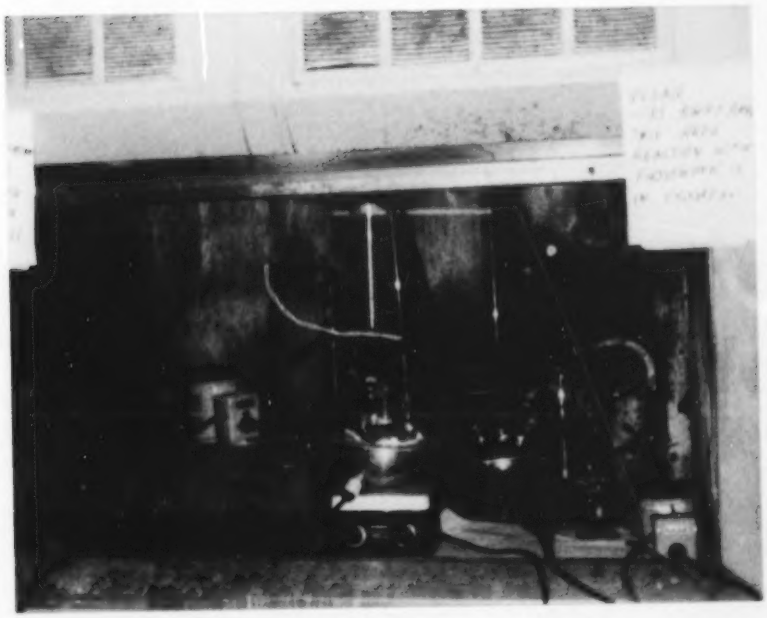


PLATE 2: Experimental Apparatus For Preparation And Reaction of Phosphine Gas With Hydrocracked Pitch

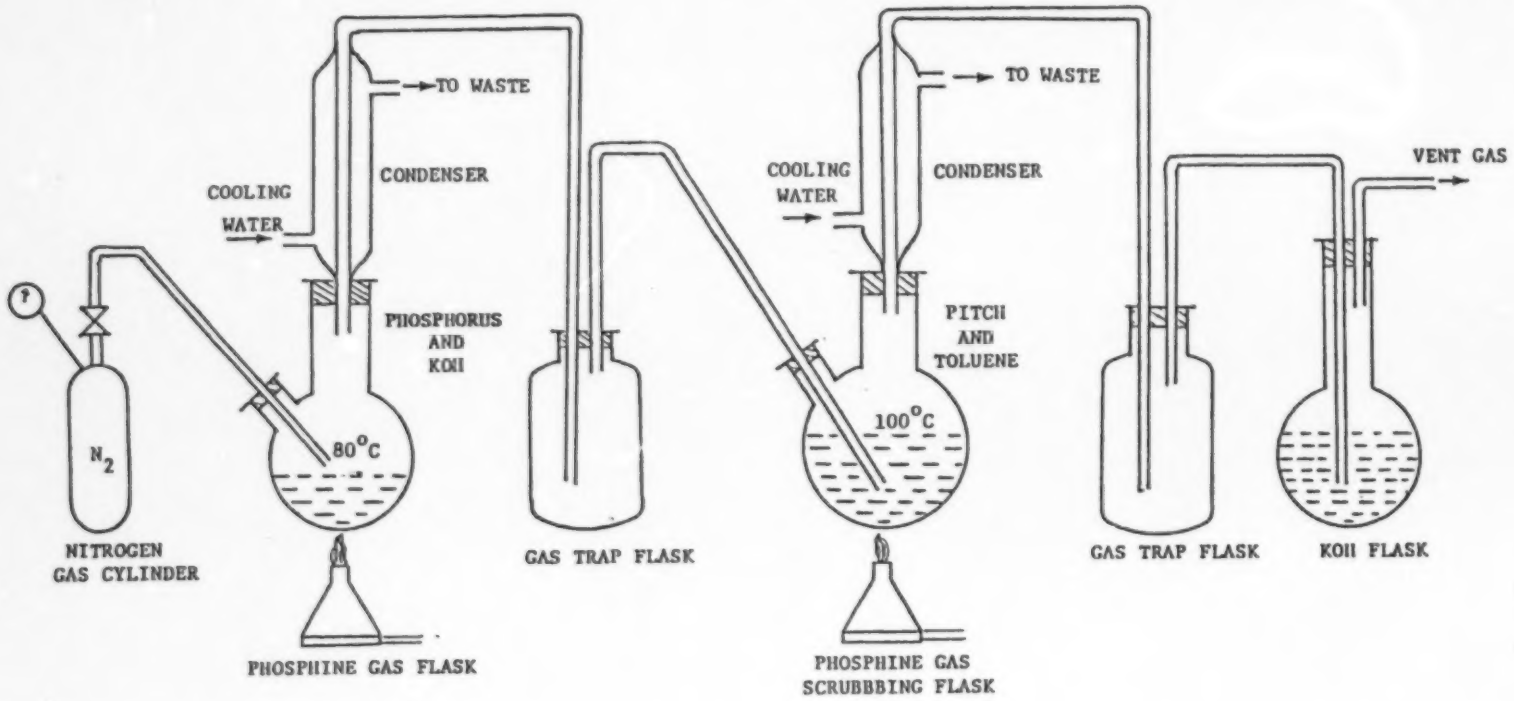


FIGURE 1: Apparatus for Preparation and Reaction of Phosphine Gas with Hydrocracked Pitch

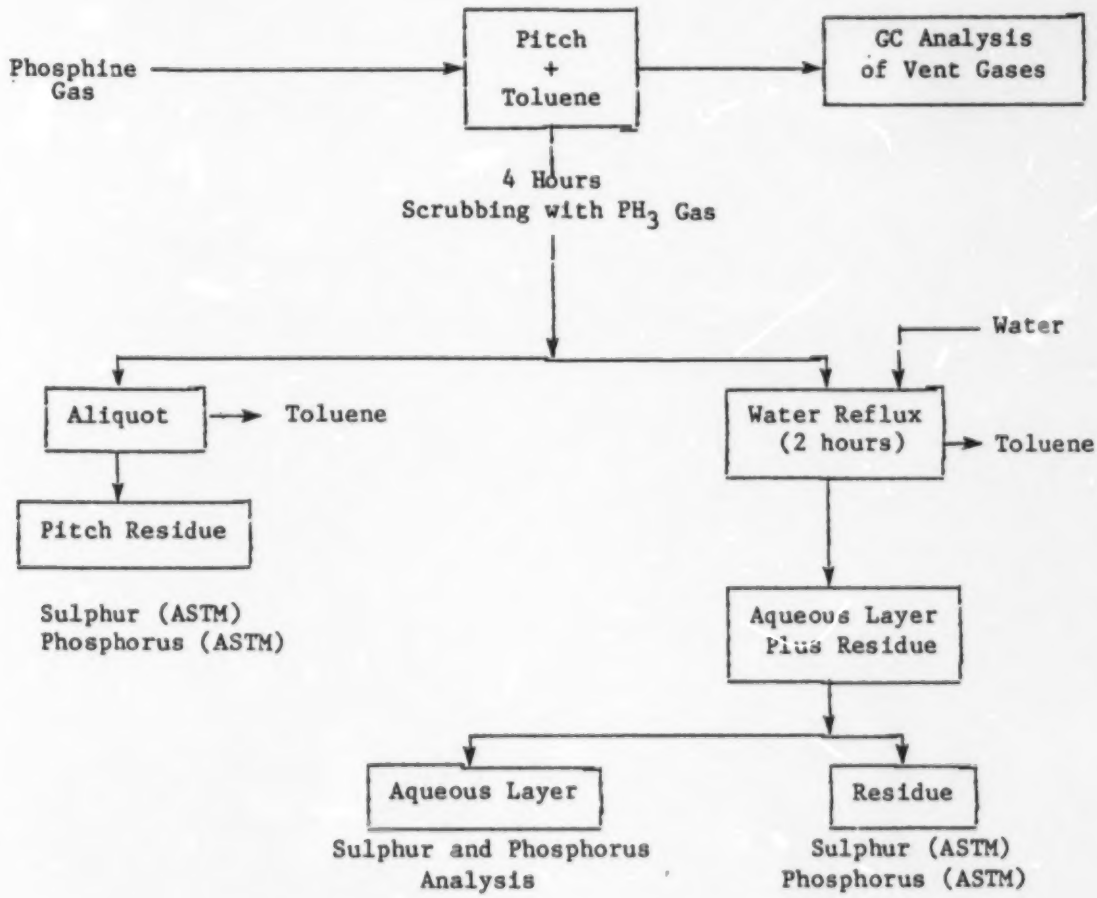
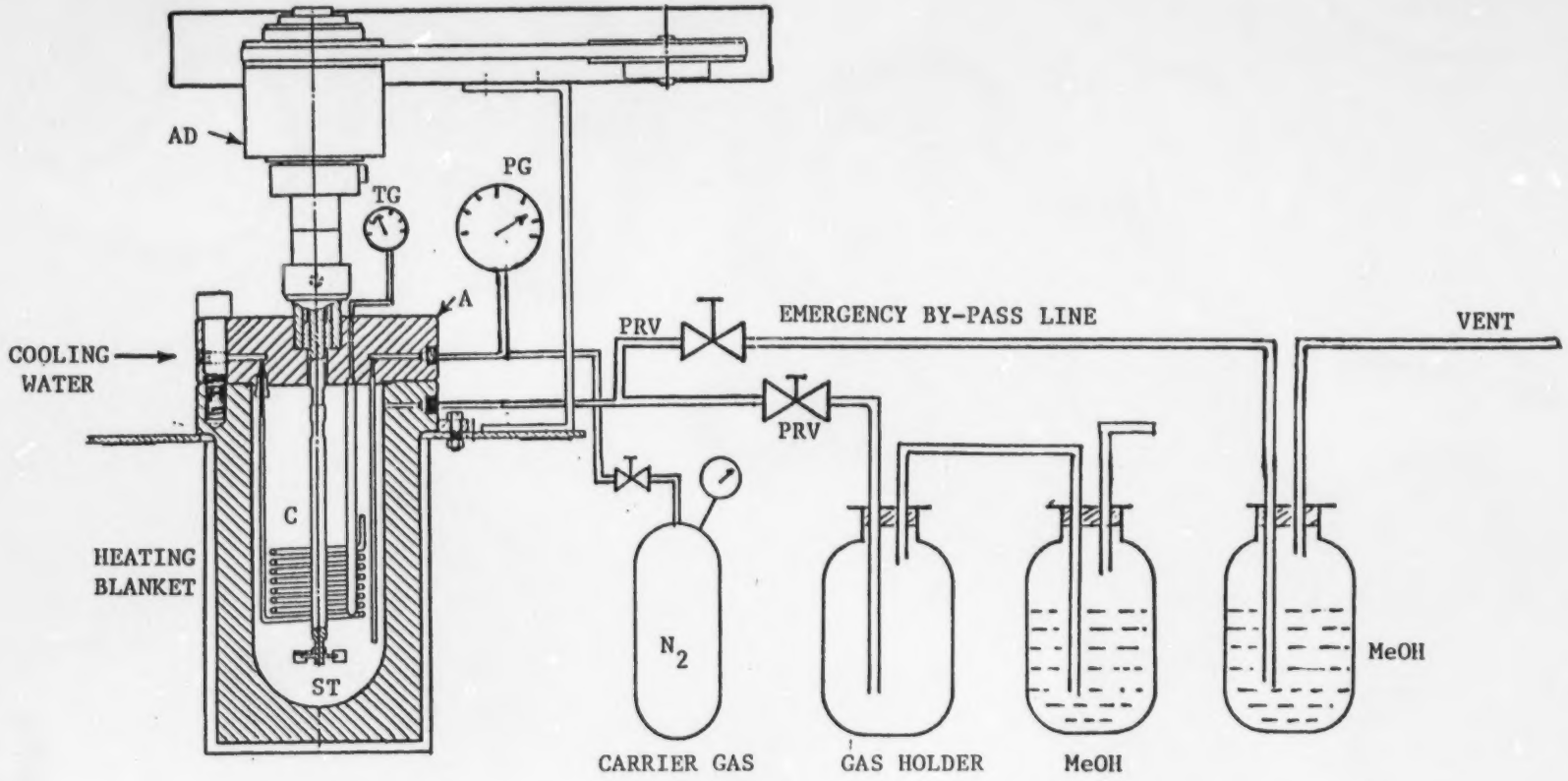


FIGURE 2: Analytical Scheme for Sulphur and Phosphorus Analysis



A	Autoclave (1-litre)
C	Cooling Coil
AD	Agitator Drive
PG	Pressure Gauge
TG	Temperature Gauge
ST	Stirrer
PRV	Pressure Reducing Valve
MeOH	Methanol

FIGURE 3: Experimental Set-Up Using An Autoclave

Table 1: Standard Free Energy of Desulphurization Reactions

	REACTION	Standard Free Energy Change ΔFo Kcal/g mole
	Reducing Agent - Hydrogen	
1	$+ 2H_2 \longrightarrow C_4H_6 + H_2S$	+ 2.2
2	$+ 3H_2 \longrightarrow C_4H_8 + H_2S$	- 17.0
3	$C_6H_5SH + H_2 \longrightarrow C_6H_6 + H_2S$	- 15.2
	Reducing Agent - Phosphine	
4	3 $+ 2\ PH_3 \longrightarrow 3C_4H_6 + P_2S_3$	- 35.9
5	3 $+ 4\ PH_3 \longrightarrow 3C_4H_8 + P_4S_3$	- 123.6
6	$6\ C_6H_5\text{-}SH + 2\ PH_3 \longrightarrow 6\ C_6H_6 + 3\ H_2S + P_2S_3$	- 133.5
7	$P_4S_3 + 9H_2 \longrightarrow 3H_3PO_2 + H_3PO_3 + 3H_2S$	- 26.0
8	$2KOH + H_2S \longrightarrow K_2S + 2H_2O$	+ 50.0

Table 2 Pyrite, Sulphate and Total Sulphur Analysis of CANMET Pitch

1.	Pyrite Sulphur (ASTM D-2492), %	0.12 0.13
2.	Sulphate Sulphur (ASTM D-2492), %	0.02 0.02
3.	Total Sulphur (ASTM D-3177)	4.12 4.17

Table 3 Summary of Blank Runs

Run Number	1
1. Experiment Conditions	
Hydrocracked Pitch, grams	100
KOH Solution (5%), ml	200
Phosphorus, grams	--
Reaction Temperature, °C	250
Reaction Time, h	1.0
2. Total Sulphur (ASTM D-3177), %	
• Before Experiment	4.12
• After Experiment	4.04
3. GC - Response	MeOH

Table 4 Summary of Desulphurization Results with Phosphine

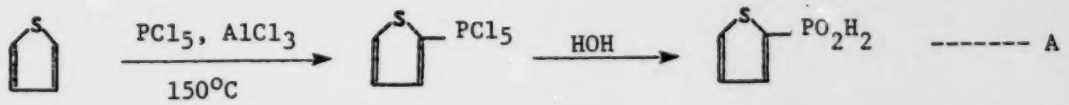
Sample	Run No. 3[1]		Run No. 4[2]	
	Sulphur (%)	Phosphorus (%)	Sulphur (%)	Phosphorus (%)
. Pitch	4.70 4.62	0.0042	4.70 4.62	0.0042
. Residue (Before water reflux)	3.87 3.88	0.012	4.26 4.33	0.0148
. Residue (After water reflux)	3.85 3.79	0.022	4.11 4.12	0.0193
. Sulphur Removal* - Before water reflux - After water reflux	 16.8 18.0		 7.8 11.7	

* Based on average values

1. 14.5% w/w phosphorus reacted with KOH
2. 13.8% w/w phosphorus reacted with KOH

Table 5 Reactions of Phosphorus and Sulphur Compounds

Phosphorylation



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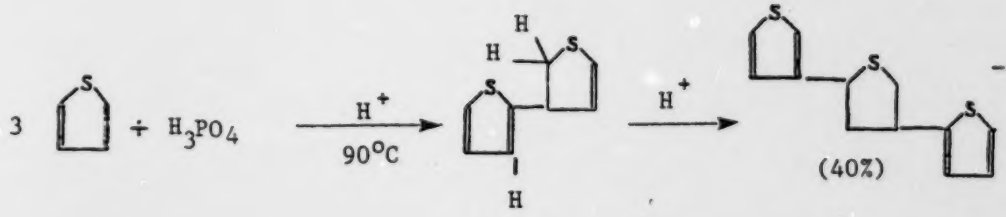

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Nucleophilic Substitution

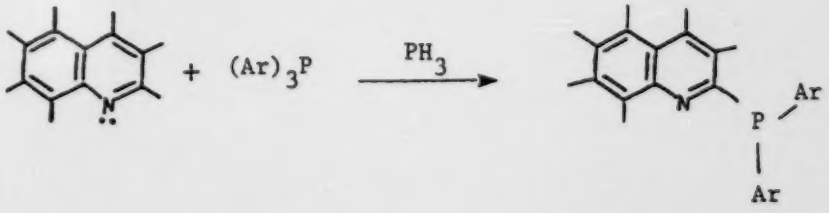

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Table 6 Summary of Desulphurization Results
Using Phosphorus at 100°C

Run No.	5	6
Total Sulphur (Before Reaction), %	4.12	4.17
Total Sulphur (After Reaction), %	3.84 3.77	3.80 3.83
Sulphur Removal*, %	7.6	8.5

* Based on average values

Table 7 Summary of Desulphurization Results Using Phosphorus at 250°C

Run No.	7	8
Total Sulphur (Before Reaction), %	4.36 4.34	4.33 4.12
Total Sulphur (After Reaction), %	4.17 3.60 -	3.81 3.93 3.73
Sulphur Removal*, %	10.6	9.7

* Based on average values

APPENDIX A

CONCORDIA UNIVERSITY RESULTS ON TOTAL SULPHUR AND PHOSPHORUS ANALYSIS

APPENDIX A

CONCORDIA UNIVERSITY RESULTS ON TOTAL SULPHUR AND PHOSPHORUS ANALYSIS

Nine Samples (2 pitch samples and 7 pitch residues) were analyzed by Science Industrial Research Unit of Concordia University for total sulphur and phosphorus content. The sample identification list is presented in Table A-1.

The three reports received from Concordia University (Report Nos. G-323, G-405, G-405A) are attached.

TABLE A-1 Sample Identification List

REPORT NO.	SAMPLE NO.	IDENTIFICATION
G-323	1-75-JS1	Run No. 7 - Total Sulphur before reaction at 250°C.
	1-77-J4	Run No. 7 - Total Sulphur after reaction at 250°C
	1-81-KSI	Run No. 8 - Total Sulphur before reaction at 250°C.
	1-82-K2	Run No. 8 - Total Sulphur after reaction at 250°C.
G-405, G-405A	1-97-CO2	Run No. 3 - Total Sulphur before reaction with phosphine gas.
	1-103-E4(TT)	Run No. 3 - Total Sulphur in the product residue.
	1-105-E10(WT)	Run No. 3 - Total Sulphur in the product residue after water reflux.
	1-112-F6(TT)	Run No. 4 - Total Sulphur in the product residue.
	1-113-EP(WT)	Run No. 4 - Total Sulphur in the product residue after water reflux.

DEPARTMENT OF CHEMISTRY

REPORT # G-323

Technitrol Ltd.
2245 St. Francois Road
Dorval, Quebec
Attention: Dr. M. Khadim

MATERIAL: Coke

RESULTS:

Sample	Sulphur
1-75-JS1	4.36%
1-77-J4	4.17%
1-81-KS1	4.33%
1-83-K2	3.81%

Robert T. Patterson
Assistant Director
Science Industrial Research Unit

RTP/ac

April 19, 1982

CONCORDIA UNIVERSITY

DEPARTMENT OF CHEMISTRY

REPORT # G-405

Technitrol Ltd.
2245 St. Francois Road
Dorval, Quebec

Attention: Dr. M. Khadim

MATERIAL: Coke

RESULTS:

Sample	Sulphur		
	Test #1	Test #2	Average
1-97-C02	4.70%	4.62%	4.66%
1-103-E4 (TT)	3.87%	3.88%	3.88%
1-105-E10 (WT)	3.85%	3.79%	3.82%
1-112-F6 (TT)	4.26%	4.33%	4.30%
1-113-FP (WT)	4.43%	4.44%	4.44%

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May 10, 1982

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CONCORDIA UNIVERSITY

DEPARTMENT OF CHEMISTRY

REPORT # G-405A

Technitrol Ltd.
2245 St. Francois Road
Dorval, Quebec

Attention: Dr. M. Khadim

MATERIAL: Coke

RESULTS:

Sample	Ash (%)	Phosphorus (as % P_2O_5 in Ash)
1-97-C02	1.13	0.85%
1-103-E4 (TT)	5.88	0.47%
1-105-E10 (WT)	5.01	0.99%
1-112-F6 (TT)	1.31	2.58%
1-113-F9 (WT)	1.30	3.40%

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APPENDIX B

NOTES ON REACTION OF PHOSPHORUS COMPOUNDS WITH PITCH

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COMPOUNDS WITH PITCH

Phosphorus compounds when reacted with thiophenes at 150°C in the presence of aluminum chloride ($AlCl_3$) produce substituted derivatives (7,8) in low yields as shown by reaction A in Table 5.

On the other hand, when 100% phosphoric acid is reacted with thiophene at 90°C, it does not cause an electrophilic or nucleophilic attack of phosphorus on sulphur atom of thiophene. Instead, a trimer of thiophene is obtained (9) as shown by reaction B in Table 5.

Phosphorus can also react with aryl systems to produce derivatives of the type $(Ar)_n P R_{3-n}$ where n may be 1, 2, or 3 and R can be H, Cl, Br or I.

Thus it is possible that the reaction of phosphine with pitch results in the production of arylphosphine type derivatives which react further to cause nucleophilic attack on the nitrogen containing groups as shown by reaction C in Table 5.

Another possibility of phosphorus addition may be through phosphorylation reactions of ortho-hydroxy functionalities. In fact, asphaltenes from bitumen have been found to undergo phosphorylation (10) with reagents such as phosphoric acid, phosphorus trichloride or phosphorus oxychloride resulting in 10 wt % increase in the phosphorus content.

It is believed that water refluxing results in the formation of phosphorus containing organic salts which remain in the residue even

Desulphurization with Phosphine (cont'd)

after toluene evaporation and thereby increasing the phosphorus content of the residue. This occurs due to the action of phosphoric acid with basic functionalities of pitch. The phosphoric acid is formed by the reaction of dissolved phosphine with water during refluxing. Because of the many possible side reactions, the stoichiometric relationship between sulphur removed and phosphorus added is difficult to correlate from the experimental data.